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The Estimation of the Elements
in the R_2O_3 Residue of a
Clay Analysis

THE ESTIMATION OF THE ELEMENTS
IN THE R_2O_3 RESIDUE OF A
CLAY ANALYSIS

BY

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FOR THE

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TABLE OF CONTENTS

I.	INTRODUCTION	PAGE 1
II.	THEORETICAL	PAGE 2
III.	PREPARATION OF KNOWN SOLUTIONS	PAGE 3
IV.	ANALYSIS OF KNOWN SOLUTIONS BY CUPFERRON METHOD	PAGE 4
V.	ANALYSIS OF ARGILLACEOUS LIMESTONE	PAGE 5
VI.	EXPERIMENTAL RESULTS	PAGE 6
VII.	CONCLUSIONS	PAGE 6
VIII.	REFERENCES	PAGE 7

CONTENTS

1	Introduction	1
2	Chapter I	2
3	Chapter II	3
4	Chapter III	4
5	Chapter IV	5
6	Chapter V	6
7	Chapter VI	7
8	Chapter VII	8
9	Chapter VIII	9
10	Chapter IX	10
11	Chapter X	11
12	Chapter XI	12
13	Chapter XII	13
14	Chapter XIII	14
15	Chapter XIV	15
16	Chapter XV	16
17	Chapter XVI	17
18	Chapter XVII	18
19	Chapter XVIII	19
20	Chapter XIX	20
21	Chapter XX	21
22	Chapter XXI	22
23	Chapter XXII	23
24	Chapter XXIII	24
25	Chapter XXIV	25
26	Chapter XXV	26
27	Chapter XXVI	27
28	Chapter XXVII	28
29	Chapter XXVIII	29
30	Chapter XXIX	30
31	Chapter XXX	31
32	Chapter XXXI	32
33	Chapter XXXII	33
34	Chapter XXXIII	34
35	Chapter XXXIV	35
36	Chapter XXXV	36
37	Chapter XXXVI	37
38	Chapter XXXVII	38
39	Chapter XXXVIII	39
40	Chapter XXXIX	40
41	Chapter XL	41
42	Chapter XLI	42
43	Chapter XLII	43
44	Chapter XLIII	44
45	Chapter XLIV	45
46	Chapter XLV	46
47	Chapter XLVI	47
48	Chapter XLVII	48
49	Chapter XLVIII	49
50	Chapter XLIX	50
51	Chapter L	51
52	Chapter LI	52
53	Chapter LII	53
54	Chapter LIII	54
55	Chapter LIV	55
56	Chapter LV	56
57	Chapter LVI	57
58	Chapter LVII	58
59	Chapter LVIII	59
60	Chapter LIX	60
61	Chapter LX	61
62	Chapter LXI	62
63	Chapter LXII	63
64	Chapter LXIII	64
65	Chapter LXIV	65
66	Chapter LXV	66
67	Chapter LXVI	67
68	Chapter LXVII	68
69	Chapter LXVIII	69
70	Chapter LXIX	70
71	Chapter LXX	71
72	Chapter LXXI	72
73	Chapter LXXII	73
74	Chapter LXXIII	74
75	Chapter LXXIV	75
76	Chapter LXXV	76
77	Chapter LXXVI	77
78	Chapter LXXVII	78
79	Chapter LXXVIII	79
80	Chapter LXXIX	80
81	Chapter LXXX	81
82	Chapter LXXXI	82
83	Chapter LXXXII	83
84	Chapter LXXXIII	84
85	Chapter LXXXIV	85
86	Chapter LXXXV	86
87	Chapter LXXXVI	87
88	Chapter LXXXVII	88
89	Chapter LXXXVIII	89
90	Chapter LXXXIX	90
91	Chapter LXXXX	91
92	Chapter LXXXXI	92
93	Chapter LXXXXII	93
94	Chapter LXXXXIII	94
95	Chapter LXXXXIV	95
96	Chapter LXXXXV	96
97	Chapter LXXXXVI	97
98	Chapter LXXXXVII	98
99	Chapter LXXXXVIII	99
100	Chapter LXXXXIX	100
101	Chapter LXXXXX	101
102	Chapter LXXXXXI	102
103	Chapter LXXXXXII	103
104	Chapter LXXXXXIII	104
105	Chapter LXXXXXIV	105
106	Chapter LXXXXXV	106
107	Chapter LXXXXXVI	107
108	Chapter LXXXXXVII	108
109	Chapter LXXXXXVIII	109
110	Chapter LXXXXXIX	110
111	Chapter LXXXXXX	111
112	Chapter LXXXXXXI	112
113	Chapter LXXXXXXII	113
114	Chapter LXXXXXXIII	114
115	Chapter LXXXXXXIV	115
116	Chapter LXXXXXXV	116
117	Chapter LXXXXXXVI	117
118	Chapter LXXXXXXVII	118
119	Chapter LXXXXXXVIII	119
120	Chapter LXXXXXXIX	120
121	Chapter LXXXXXXX	121
122	Chapter LXXXXXXXI	122
123	Chapter LXXXXXXXII	123
124	Chapter LXXXXXXXIII	124
125	Chapter LXXXXXXXIV	125
126	Chapter LXXXXXXXV	126
127	Chapter LXXXXXXXVI	127
128	Chapter LXXXXXXXVII	128
129	Chapter LXXXXXXXVIII	129
130	Chapter LXXXXXXXIX	130
131	Chapter LXXXXXXXI	131
132	Chapter LXXXXXXXII	132
133	Chapter LXXXXXXXIII	133
134	Chapter LXXXXXXXIV	134
135	Chapter LXXXXXXXV	135
136	Chapter LXXXXXXXVI	136
137	Chapter LXXXXXXXVII	137
138	Chapter LXXXXXXXVIII	138
139	Chapter LXXXXXXXIX	139
140	Chapter LXXXXXXXI	140
141	Chapter LXXXXXXXII	141
142	Chapter LXXXXXXXIII	142
143	Chapter LXXXXXXXIV	143
144	Chapter LXXXXXXXV	144
145	Chapter LXXXXXXXVI	145
146	Chapter LXXXXXXXVII	146
147	Chapter LXXXXXXXVIII	147
148	Chapter LXXXXXXXIX	148
149	Chapter LXXXXXXXI	149
150	Chapter LXXXXXXXII	150
151	Chapter LXXXXXXXIII	151
152	Chapter LXXXXXXXIV	152
153	Chapter LXXXXXXXV	153
154	Chapter LXXXXXXXVI	154
155	Chapter LXXXXXXXVII	155
156	Chapter LXXXXXXXVIII	156
157	Chapter LXXXXXXXIX	157
158	Chapter LXXXXXXXI	158
159	Chapter LXXXXXXXII	159
160	Chapter LXXXXXXXIII	160
161	Chapter LXXXXXXXIV	161
162	Chapter LXXXXXXXV	162
163	Chapter LXXXXXXXVI	163
164	Chapter LXXXXXXXVII	164
165	Chapter LXXXXXXXVIII	165
166	Chapter LXXXXXXXIX	166
167	Chapter LXXXXXXXI	167
168	Chapter LXXXXXXXII	168
169	Chapter LXXXXXXXIII	169
170	Chapter LXXXXXXXIV	170
171	Chapter LXXXXXXXV	171
172	Chapter LXXXXXXXVI	172
173	Chapter LXXXXXXXVII	173
174	Chapter LXXXXXXXVIII	174
175	Chapter LXXXXXXXIX	175
176	Chapter LXXXXXXXI	176
177	Chapter LXXXXXXXII	177
178	Chapter LXXXXXXXIII	178
179	Chapter LXXXXXXXIV	179
180	Chapter LXXXXXXXV	180
181	Chapter LXXXXXXXVI	181
182	Chapter LXXXXXXXVII	182
183	Chapter LXXXXXXXVIII	183
184	Chapter LXXXXXXXIX	184
185	Chapter LXXXXXXXI	185
186	Chapter LXXXXXXXII	186
187	Chapter LXXXXXXXIII	187
188	Chapter LXXXXXXXIV	188
189	Chapter LXXXXXXXV	189
190	Chapter LXXXXXXXVI	190
191	Chapter LXXXXXXXVII	191
192	Chapter LXXXXXXXVIII	192
193	Chapter LXXXXXXXIX	193
194	Chapter LXXXXXXXI	194
195	Chapter LXXXXXXXII	195
196	Chapter LXXXXXXXIII	196
197	Chapter LXXXXXXXIV	197
198	Chapter LXXXXXXXV	198
199	Chapter LXXXXXXXVI	199
200	Chapter LXXXXXXXVII	200
201	Chapter LXXXXXXXVIII	201
202	Chapter LXXXXXXXIX	202
203	Chapter LXXXXXXXI	203
204	Chapter LXXXXXXXII	204
205	Chapter LXXXXXXXIII	205
206	Chapter LXXXXXXXIV	206
207	Chapter LXXXXXXXV	207
208	Chapter LXXXXXXXVI	208
209	Chapter LXXXXXXXVII	209
210	Chapter LXXXXXXXVIII	210
211	Chapter LXXXXXXXIX	211
212	Chapter LXXXXXXXI	212
213	Chapter LXXXXXXXII	213
214	Chapter LXXXXXXXIII	214
215	Chapter LXXXXXXXIV	215
216	Chapter LXXXXXXXV	216
217	Chapter LXXXXXXXVI	217
218	Chapter LXXXXXXXVII	218
219	Chapter LXXXXXXXVIII	219
220	Chapter LXXXXXXXIX	220
221	Chapter LXXXXXXXI	221
222	Chapter LXXXXXXXII	222
223	Chapter LXXXXXXXIII	223
224	Chapter LXXXXXXXIV	224
225	Chapter LXXXXXXXV	225
226	Chapter LXXXXXXXVI	226
227	Chapter LXXXXXXXVII	227
228	Chapter LXXXXXXXVIII	228
229	Chapter LXXXXXXXIX	229
230	Chapter LXXXXXXXI	230
231	Chapter LXXXXXXXII	231
232	Chapter LXXXXXXXIII	232
233	Chapter LXXXXXXXIV	233
234	Chapter LXXXXXXXV	234
235	Chapter LXXXXXXXVI	235
236	Chapter LXXXXXXXVII	236
237	Chapter LXXXXXXXVIII	237
238	Chapter LXXXXXXXIX	238
239	Chapter LXXXXXXXI	239
240	Chapter LXXXXXXXII	240
241	Chapter LXXXXXXXIII	241
242	Chapter LXXXXXXXIV	242
243	Chapter LXXXXXXXV	243
244	Chapter LXXXXXXXVI	244
245	Chapter LXXXXXXXVII	245
246	Chapter LXXXXXXXVIII	246
247	Chapter LXXXXXXXIX	247
248	Chapter LXXXXXXXI	248
249	Chapter LXXXXXXXII	249
250	Chapter LXXXXXXXIII	250
251	Chapter LXXXXXXXIV	251
252	Chapter LXXXXXXXV	252
253	Chapter LXXXXXXXVI	253
254	Chapter LXXXXXXXVII	254
255	Chapter LXXXXXXXVIII	255
256	Chapter LXXXXXXXIX	256
257	Chapter LXXXXXXXI	257
258	Chapter LXXXXXXXII	258
259	Chapter LXXXXXXXIII	259
260	Chapter LXXXXXXXIV	260
261	Chapter LXXXXXXXV	261
262	Chapter LXXXXXXXVI	262
263	Chapter LXXXXXXXVII	263
264	Chapter LXXXXXXXVIII	264
265	Chapter LXXXXXXXIX	265
266	Chapter LXXXXXXXI	266
267	Chapter LXXXXXXXII	267
268	Chapter LXXXXXXXIII	268
269	Chapter LXXXXXXXIV	269
270	Chapter LXXXXXXXV	270
271	Chapter LXXXXXXXVI	271
272	Chapter LXXXXXXXVII	272
273	Chapter LXXXXXXXVIII	273
274	Chapter LXXXXXXXIX	274
275	Chapter LXXXXXXXI	275
276	Chapter LXXXXXXXII	276
277	Chapter LXXXXXXXIII	277
278	Chapter LXXXXXXXIV	278
279	Chapter LXXXXXXXV	279
280	Chapter LXXXXXXXVI	280
281	Chapter LXXXXXXXVII	281
282	Chapter LXXXXXXXVIII	282
283	Chapter LXXXXXXXIX	283
284	Chapter LXXXXXXXI	284
285	Chapter LXXXXXXXII	285
286	Chapter LXXXXXXXIII	286
287	Chapter LXXXXXXXIV	287
288	Chapter LXXXXXXXV	288
289	Chapter LXXXXXXXVI	289
290	Chapter LXXXXXXXVII	290
291	Chapter LXXXXXXXVIII	291
292	Chapter LXXXXXXXIX	292
293	Chapter LXXXXXXXI	293
294	Chapter LXXXXXXXII	294
295	Chapter LXXXXXXXIII	295
296	Chapter LXXXXXXXIV	296
297	Chapter LXXXXXXXV	297
298	Chapter LXXXXXXXVI	298
299	Chapter LXXXXXXXVII	299
300	Chapter LXXXXXXXVIII	300
301	Chapter LXXXXXXXIX	301
302	Chapter LXXXXXXXI	302
303	Chapter LXXXXXXXII	303
304	Chapter LXXXXXXXIII	304
305	Chapter LXXXXXXXIV	305
306	Chapter LXXXXXXXV	306
307	Chapter LXXXXXXXVI	307
308	Chapter LXXXXXXXVII	308
309	Chapter LXXXXXXXVIII	309
310	Chapter LXXXXXXXIX	310
311	Chapter LXXXXXXXI	311
312	Chapter LXXXXXXXII	312
313	Chapter LXXXXXXXIII	313
314	Chapter LXXXXXXXIV	314
315	Chapter LXXXXXXXV	315
316	Chapter LXXXXXXXVI	316
317	Chapter LXXXXXXXVII	317
318	Chapter LXXXXXXXVIII	318
319	Chapter LXXXXXXXIX	319
320	Chapter LXXXXXXXI	320
321	Chapter LXXXXXXXII	321
322	Chapter LXXXXXXXIII	322
323	Chapter LXXXXXXXIV	323
324	Chapter LXXXXXXXV	324
325	Chapter LXXXXXXXVI	325
326	Chapter LXXXXXXXVII	326
327	Chapter LXXXXXXXVIII	327
328	Chapter LXXXXXXXIX	328
329	Chapter LXXXXXXXI	329
330	Chapter LXXXXXXXII	330
331	Chapter LXXXXXXXIII	331
332	Chapter LXXXXXXXIV	332
333	Chapter LXXXXXXXV	333
334	Chapter LXXXXXXXVI	334
335	Chapter LXXXXXXXVII	335
336	Chapter LXXXXXXXVIII	336
337	Chapter LXXXXXXXIX	337
338	Chapter LXXXXXXXI	338
339	Chapter LXXXXXXXII	339
340	Chapter LXXXXXXXIII	340
341	Chapter LXXXXXXXIV	341
342	Chapter LXXXXXXXV	342
343	Chapter LXXXXXXXVI	343
344	Chapter LXXXXXXXVII	344
345	Chapter LXXXXXXXVIII	345
346	Chapter LXXXXXXXIX	346
347	Chapter LXXXXXXXI	347
348	Chapter LXXXXXXXII	348
349	Chapter LXXXXXXXIII	349
350	Chapter LXXXXXXXIV	350
351	Chapter LXXXXXXXV	351
352	Chapter LXXXXXXXVI	352
353	Chapter LXXXXXXXVII	353
354	Chapter L	

THE ESTIMATION OF THE ELEMENTS IN THE $R_2 O_3$ RESIDUE
OF A CLAY ANALYSIS

I. INTRODUCTION

The use of cupferron, ammonium nitrosophenylhydroxylamine, as a precipitant for iron was suggested by Oskar Baudisch in 1909, (3). Since then various investigators have used it in quantitative analyses and the results have been excellent in each case. It seems, however, that the value of this reagent in quantitative analysis has not been fully recognized and the present investigation was undertaken to determine its value in ordinary clay analyses. The work consisted of the preparation of known solutions and their analysis by the cupferron method and an analysis of a standard argillaceous limestone sample by the usual method and by the cupferron method.

II. THEORETICAL

Cupferron precipitates iron, titanium, vanadium, zirconium, cerium and copper quantitatively. All these are precipitated from strongly acid solutions except the copper. The fact that copper does not precipitate in acid solution furnishes a method for its separation from iron, (3). The separation of these elements from aluminium, manganese, chromium, nickel, cobalt, zinc, the alkali earths and phosphoric and arsenic acids has been found to be quantitative.

James Brown has shown that cupferron can be used for the analysis of zircon and baddeleyite, (4), and his method was followed in the cupferron analysis. The R_2O_3 precipitate of a clay analysis may contain iron, aluminium, titanium, zirconium, chromium, vanadium, phosphorous, the rare earths and manganese if all these are present in the sample. The other elements may be separated from manganese by precipitation in the presence of large amounts of ammonium chloride in case the amount of manganese is small. The cupferron separation depends on the fact that the iron, titanium, zirconium and vanadium are precipitated while the other elements are not. Various methods may then be used for the separation of the elements present in the precipitate and filtrate.

III. PREPARATION OF KNOWN SOLUTIONS

The first experimental work undertaken was the preparation of solutions of iron, aluminium, titanium and manganese, their determination by ordinary methods and then the separation by means of cupferron. The solutions were made up as follows:

Substance	Weight	Volume of solution	Approximate weight of oxide per cc.
Fe ₂ (SO ₄) ₃	2.5745gm	460cc	.002235gm Fe ₂ O ₃
Al ₂ (SO ₄) ₃	2.0923gm	470cc	.001329gm Al ₂ O ₃
K ₂ Ti F ₆	1.1133gm	480cc	.000773gm Ti O ₂
Mn SO ₄	1.3672gm	480cc	.001339gm Mn O

Each of these solutions were then analysed to find the true weight of the element present. The iron, aluminium and titanium were precipitated by means of ammonium hydroxide and ignited to the oxide, (2). The manganese was precipitated and weighed as the pyrophosphate, (2).

Nature of precipitate	Volume of solution	Weight of precipitate	Weight of oxide per cc.
Fe ₂ O ₃	50cc	.1097gm .1095gm	.002192gm
Al ₂ O ₃	50cc	.0650gm .0653gm	.001303gm
Ti O ₂	50cc	.0385gm .0386gm	.000771gm
Mn ₂ P ₂ O ₇	25cc	.0656gm .0657gm	.001313gm

A solution containing all four of these elements was next made up as follows:

Volume	Solution of	Weight of oxide
200cc	iron	.4384gm
120cc	aluminium	.1564gm
40cc	Titanium	.0308gm
40cc	manganese	.0525gm

IV. ANALYSIS OF KNOWN SOLUTION BY CUPFERRON METHOD

For the analysis, 100cc of the known solution was used. This was equal to a solution of these four elements from one gram of a sample containing 10.96% Fe_2O_3 , 3.91% Al_2O_3 , .77% TiO_2 and 1.31% MnO .

1. Precipitation of iron and titanium by means of cupferron, (4).

Treat the solution with ammonium hydroxide in slight excess. Add 1:1 sulphuric acid in slight excess and then add 25cc more. Dilute the solution to 150cc and cool with ice. Add 100cc of a 6% aqueous cupferron solution, slowly with constant stirring and filter immediately. Wash 20 times with 1:9 hydrochloric acid. Wash with dilute ammonia until the washings become colorless. Partly dry the precipitate at 80°C ., and ignite in a platinum crucible. The ignited precipitate gives the weight of the iron and titanium oxides.

2. Determination of iron and titanium, (1).

The oxides were fused with potassium pyrosulfate and dissolved in sulphuric acid. The iron was determined volumetrically by means of potassium permanganate after reduction with hydrogen sulfide. The titanium was determined by difference.

3. Determination of aluminium and manganese, (4), (2).

Evaporate the filtrate from the cupferron precipitation to about 25cc with 4 50cc portions of concentrated nitric acid. Dilute to 300cc. Precipitate the aluminium by means of ammonium chloride and ammonium hydroxide. Three precipitations were made. The manganese was determined in the filtration by titration against permanganate solution.

V. ANALYSIS OF ARGILLACEOUS LIMESTONE

1. Method of analysis of the U. S. Geological Survey Bulletin #700, (1).

The sample used was sample #1 of the U. S. Bureau of Standards, an argillaceous limestone. The silica was determined in the usual way. The iron, titanium, aluminium and phosphorous were precipitated without manganese in the presence of a large amount of ammonium chloride. The iron was determined volumetrically and the titanium colorimetrically. The combined aluminium and phosphorous were determined by difference.

2. By the cupferron method, (4).

The silica was removed as in the previous analysis. The residue remaining after treatment of the silica with sulphuric and hydrofluoric acids was fused with .5gm of potassium pyrosulphate and the fused mass dissolved in sulphuric acid. This solution was then added to the main solution. The iron, titanium, aluminium and phosphorous were precipitated as hydroxides, (1). After one precipitation the precipitate was dissolved in 100cc 1:7 sulphuric acid. The filtrate was evaporated to a slight precipitate, being kept alkaline with ammonium hydroxide. The precipitate was filtered off and added to the main precipitate. The filtrate was used for the determination of manganese. The iron and titanium were then precipitated from the sulfuric acid solution as in IV, 1 & 2. The aluminium was then determined as in IV, 3 and the filtrate used for the determination of manganese. The weight of residual silica was determined by the treatment of the aluminium oxide with sulphuric and hydrofluoric acids.

VI. EXPERIMENTAL RESULTS

1. Results of the analysis of known solution by cupferron method.

Analysis for	Weight of oxide taken	Weight of oxide found	
Fe ₂ O ₃	.1096gm	.1094gm	.1095gm
Ti O ₂	.0077gm	.0079gm	.0080gm
Al ₂ O ₃	.0391gm	.0389gm	.0388gm
Mn O	.0131gm	.0127gm	.0125gm

2. Results of the analysis of limestone

Analysis for	Bureau of Standards	Ordinary Method		Cupferron Method	
Si O ₂	18.15%	18.13%	18.09%	18.16%	18.18%
Fe ₂ O ₃	1.72%	1.70%	1.76%	1.73%	1.72%
Ti O ₂	.22%	.24%	.24%	.24%	.23%
Al ₂ O ₃ *	5.88%	5.92%	5.97%	5.91%	5.93%
Mn O	.04%	.06%	.06%	.04%	.06%

* including P₂ O₅

VII. CONCLUSIONS

It appears that the cupferron method is superior to the ordinary method in that it gives a more direct determination of aluminium and obviates the necessity for determining the latter by difference as it is usually determined. The phosphorous is determined in a separate sample and for the true percent of aluminium this must be subtracted from the figures obtained. The cupferron method also obviates the long pyrophosphate fusion involved in the ordinary method and the contamination of the solution with platinum.

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